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(54) **Foam detergent composition with enzymes**

(57) The present invention relates to a cleaning composition, in the form of a low density foam, which comprises a surfactant system and enzymes. The cleaning composition comprises from 0.0001% to 0.005% pure protease enzyme protein by weight of the total foam composition. The invention also relates to a packaged product for dispensing the foam, preferably an aerosol package, as well as to a method for cleaning textile fabrics using the foam.

EP 0 839 905 A1

Description

The present invention relates to a cleaning composition, in the form of a foam, which comprises a surfactant system and enzymes. The invention also relates to a packaged product for dispensing the foam, preferably an aerosol package, as well as to a method for cleaning textile fabrics using the foam.

Enzymes have been used for many years in both granular and liquid laundry detergents. The Applicant's copending European patent application number 96201705.9, filed on 19th June 1996, claims detergent compositions comprising from 0.0001% to 0.5% by weight of pure protease enzyme protein.

Alternative forms of providing laundry detergents are now being considered.

EP-A-0 677 577, published on 18th October 1995, discloses a foaming detergent composition for cleaning textile fabrics which may comprise enzymes such as protease, alcalase, lipase, cellulase.

It has now been found that enzymatic activity provided by a foamed laundry detergent is much greater than that provided by either a comparable granular or liquid laundry detergent having the same enzyme system (weight for weight).

The present invention is concerned with a means of delivering a foam comprising enzymes which is both highly efficient and cost-effective. It is an objective of the present invention to provide a foam detergent to enhance the appearance of the fabric surface without causing unacceptable wear or tensile strength loss of the fabric. It is a further objective of the present invention to provide a foaming composition with good enzyme stability.

Summary of the Invention

According to the invention these objects are achieved by a foam composition comprises from 0.0001% to 0.005% pure protease enzyme protein by weight of the total foam composition.

In a preferred embodiment of the present invention the foam composition further comprises 0.00001% to 0.0005%, and more preferably from 0.00005% to 0.00025%, pure cellulase enzyme protein by weight of the total foam composition.

In a further embodiment of the invention the foam composition is dispensed from a packaged product comprising a sealed container, preferably an aerosol can; and a dispensing means, preferably a foam dispensing nozzle; and further comprising a propellant gas, wherein the propellant gas comprises carbon dioxide, nitrous oxides, air or mixtures thereof. Carbon dioxide is most preferred.

In a further aspect of the invention a method of cleaning textile fabrics is provided, comprising the steps of:

- (i) forming a foam composition as defined above,
- (ii) dissolving or dispersing the foam in water to form an aqueous solution; and
- either subsequently or simultaneously
- (iii) agitating the cleaned textile fabrics in the aqueous solution.

Detailed Description of the Invention

Foam is a coarse dispersion of gas in a relatively small amount of liquid. The foams of the present invention are a continuous liquid phase comprising a composition, and a dispersed phase comprising a gas. Typically, the gas "bubbles" of the dispersed phase can vary in size from 50 micrometers to several millimetres.

In general, the quality of the foam is determined by assessing various foam quality attributes, such as 1) the appearance of the foam as it is determined by the uniformity of the bubble size distribution, as well as by the actual bubble sizes, wherein small and uniformly sized bubbles are generally preferred; 2) the thickness of the foam as it is determined by the apparent foam viscosity, wherein a greater apparent foam viscosity is generally preferred; 3) the density of the foam which is preferably less than 250g/l, more preferably less than 150 g/l, and most preferably less than 100 g/l; and 4) the drainage of the liquid from the foam upon standing on a solid surface, wherein slow drainage of the liquid is generally preferred.

Preferred components of the detergent foam will now be described in more detail.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ethanolamine, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the ethanolamine, sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., monoethanolamine, sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ethanolamine, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group

containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383; and methyl ester sulphonates. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁-C₁₃ LAS.

Other anionic surfactants herein are the alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; coconut oil fatty acid monoglyceride sulfonates and sulfates; salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and salts of alkyl ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; watersoluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful as surfactants in the compositions of the invention. Indeed, preferred processes use anionic/nonionic blends. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 1 to 25 moles of ethylene oxide per mole of alcohol, especially 2 to 7 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms; and condensation products of propylene glycol with ethylene oxide.

Other preferred nonionics are polyhydroxy fatty acid amides which may be prepared by reacting a fatty acid ester and an N-alkyl polyhydroxy amine. The preferred amine for use in the present invention is N-(R₁)-CH₂(CH₂OH)₄-CH₂OH and the preferred ester is a C₁₂-C₂₀ fatty acid methyl ester. Most preferred is the reaction product of N-methyl glucamine (which may be derived from glucose) with C₁₂-C₂₀ fatty acid methyl ester.

Methods of manufacturing polyhydroxy fatty acid amides have been described in WO 9206073, published on April, 1992. This application describes the preparation of polyhydroxy fatty acid amides in the presence of solvents. A highly preferred embodiment of the invention N-methyl glucamine is reacted with a C₁₂-C₂₀ methyl ester.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be either straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the form R₄R₅R₆R₇N⁺X⁻ wherein R₄ is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and R₅, R₆ and R₇ are each C₁-C₄ alkyl preferably methyl; X⁻ is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include C₁₂-C₂₀ methyl ester.

alkyl trimethyl ammonium chloride and cocalkyl trimethyl ammonium methosulfate.

Other surfactants that may be used in the compositions of the present invention include C10-C18 glycerol ethers, C10-18 alkyl polyglycoside and their corresponding sulphated polyglycosides, alkyl ester sulphonates, and oleoyl sarcosinate.

Proteolytic enzymes

The proteolytic enzymes are incorporated in the detergent compositions of the present invention at a level of from 0.0001% to 0.005%, preferably from 0.0002% to 0.002%, more preferably from 0.0005% to 0.001% pure protease enzyme protein by weight of the composition.

The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or non purified forms of this enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM™ (protein engineered Maxacal) from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. Other preferred proteases include those of WO 95/10591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637.

Preferred protease for use in the present invention are SAVINASE® and the proteases described in EP 215 446 and WO 95/10591 at a level of from 0.0001% to 0.005%, preferably from 0.0002% to 0.002%, more preferably 0.0005% to 0.001% pure protease enzyme protein by weight of total composition in foam detergent compositions.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 93/07263 A and WO 93/07260 A to Genencor International, WO 89/08694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for foam detergent formulations are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 94/01532 A to Novo.

The detergent compositions can in addition to and protease enzymes further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, gluco-amylases, amylases, xylanases, lipases, esterases, cutinases, pectinases, reductases, oxidases, phenoloxidases, lipoxigenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al.

which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase.

Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.00001% to 0.001%, preferably 0.00005% to 0.00025% of active enzyme protein by weight of the detergent composition. (These levels correspond to 0.005 CEVU/g to 0.2 CEVU/g, preferably 0.02 CEVU/g to 0.1 CEVU/g).

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Suitable cutinases are described in WO 94/14963 and WO 94/14964. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO/94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. Other amylases known for use in detergent compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Examples of commercial α -amylases products are Termamyl[®], Ban[®] and Fungamyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases: α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas α -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in the copending European patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

The foam of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ethanolamine, ammonium or substituted ammonium chlorides, fluorides and sulfates. The sodium, ethanolamine and ammonium salts of the above are preferred. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the present invention.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ethanolamine, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhydroxyso-

fonates. Preferred are the sodium, ethanolamine and ammonium salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the salts of ethylene diphosphonic acid, the salts of ethane 1-hydroxy-1,1-diphosphonic acid and the salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference. In general, however, phosphates are preferably avoided for environmental reasons.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4.

Another component of the foaming compositions useful herein comprises nonaqueous, viscosity by reducing, organic solvent (s). The term "solvent" is used herein to connote non-surface active or low surface active materials that dissolve into the detergent composition matrix having a viscosity reduction effect on the composition. This effect is generally a result of their interaction with the surfactant-water system present in the formulations preventing the formulation of liquid crystal phases. The term "solvent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto.

The non-aqueous organic materials which are employed as solvents herein can be liquids of high or low polarity. High polarity liquids, suitable as solvents are for example short chain alcohols (ethanol, propanol, propane-diol, etc), short chain aldehydes (methylal, acetaldehyde, etc), short chain ketones (acetone, propanone, etc) and short chain ethers.

Other polar materials useful in some cases are glycerols, glycols and short chain ethoxylated alcohols (short chain non-ionic surfactants)

The short chain nonionic surfactants for use herein are alkoxyated alcohols according to the formula :



wherein R is a C6 to C10 straight or branched, hydrocarbon chain and n, representing the average ethoxylation degree, is from 1 to 10, or mixtures thereof. A is ethylene oxide or propylene oxide or mixtures thereof.

Suitable surfactants for use herein can readily be made by condensing alcohols having the desired chain length with propylene or ethylene oxide, or mixtures thereof. Suitable short chain alkoxyated for use herein are commercially available from several suppliers, for example Dehydrol O4[®] from Henkel (C8EO4), Mergital C4[®] from Sidobre (C8EO4), and Imbentin AG/810/050[®] and AG/810/080[®] from Kolb (respectively C8-10EO5 and C8-10EO8).

Suitable types of low-polarity solvents useful in the nonaqueous liquid detergent compositions herein include alkylene glycol mono lower alkyl ethers, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

A preferred type of nonaqueous, low-polarity solvent for use herein comprises the mono-, di-, tri-, or tetra-C₂-C₃ alkylene glycol mono C₂-C₆ alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred.

Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve. Another preferred type of nonaqueous, low-polarity organic solvent useful herein comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

Yet another preferred type of non-polar, nonaqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula : $\text{R}^1\text{-C(O)-OCH}_3$ wherein R^1 ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The nonaqueous, organic solvent(s) employed should, of course, be compatible and non-reactive with other composition components, used in the foaming compositions herein. Such a solvent component will generally be utilized in an amount of from about 1% to 60% by weight of the composition. More preferably, the nonaqueous, organic solvent will comprise from about 5% to 40% by weight of the composition, most preferably from about 10% to 25% by weight of the composition.

Foam stabilising agents may also be employed in the compositions of the present invention. Especially preferred are aliphatic alcohols such as straight chain saturated alcohols of 12 to 18 carbon atoms e.g. cetyl alcohol, stearyl alcohol, myristyl alcohol and mixtures thereof. Polymers including polyvinylpyrrolidone, polyvinyl alcohol, polyacrylamide, polypeptides, polysaccharides, cellulose derivatives; and also natural and synthetic gums and resins such as guar gum, xanthan gum, carageenan, sodium alginate and caseinate may also be used in the present invention.

Textile fabrics are any materials made from cloth, including garments such as shirts, blouses, socks, skirts, trou-

sers, jackets, underwear etc, and also including tablecloths, towels, curtains etc. The definition of textile fabrics as used herein does not include carpets and similar floor coverings.

Textile fabrics which are to be used in the present invention are commonly made by weaving or knitting. Many different fibres may be used to produce woven, knitted or other types of textile fabric including synthetic fibres (such as polyester, polyamide, etc.) and natural fibres from plants (such as cotton, hemp) and from animals (such as wool, angora, silk). Blends of different fibres are also commonly used.

It is important to distinguish between the foam of the present invention and the suds which are commonly encountered in everyday washing process. The foam of the present invention is much more concentrated and comprises less water than conventional suds. The foam of the present invention preferably comprises less than 25%, and more preferably less than 15% by weight of water. The foam of the present invention preferably comprises at least 18% by weight, and more preferably at least 25% by weight of a surface active agent. Most preferred foams for use as cleaning compositions comprise at least 10% by weight, preferably at least 20% by weight of anionic surfactant.

On the other hand, suds, which are formed in conventional washing process when detergents are diluted prior to washing, are formed from quite dilute solutions typically 100g of product in 10 litres of water. The result is a wash liquor which comprises about 99% by weight of water. A layer of suds may form on the surface of the wash liquor, the composition of the suds being similar to that of the wash liquor itself. The surfactant content of the suds will normally be much less than 1%, typically less than 0.3%. Consequently the difference between the foam of the present invention and the suds of a conventional washing process will be understood.

It will also be recognised by the man skilled in the art that suds are often considered undesirable in the washing process and antisuds agents are often employed to reduce or control them. In a washing process in which the solution of detergent active agents is the medium of transport of the actives to the fibre surface, the presence of suds can diminish washing performance. This is because the detergent actives which are in the suds are no longer dissolved in the washing liquor itself, and are not therefore efficiently transported to the fibre surface.

The packaged product of the present invention comprises a sealed container, such as an essentially cylindrical bottle, having a dispensing means such as a nozzle. The container contains the composition and propellant gas.

Suitable containers may be made from any material, especially aluminium, tin-plate, plastics including PET, OPP, PE or polyamide and including mixtures, laminates or other combinations of these. Foam is dispensed when the nozzle is activated and the detergent is released together with the propellant gas. The propellant gas expands to form many "bubbles" within the composition thereby creating the foam.

Propellant gas

The propellant gas of the present invention comprises either liquid propellants or compressed gas propellants. Examples of liquid propellants are fluorocarbons, chlorofluorocarbons, H-chlorofluorocarbons, methane, ethane, propane, butane, pentane. Examples of compressed gas propellants are carbon dioxide, nitrogen or nitrous oxides (especially N₂O), air, ammonia and dimethyl ether. Most preferred is carbon dioxide because of environmental and flammability considerations.

Various ways to pressurise the propellant gas are known in the art. For example the gas may be pressurised at the time of packing. The product may be physically separated from a compressed gas by a membrane such as rubber under tension. Alternatively a means for pressurising the gas subsequently by mechanical action may be provided (so-called "pump and spray" systems).

Various apparatus for delivering foams are described in US-A 5 364 031 issued on 15th November 1994 entitled "Foam Dispensing Nozzles and Dispensers Employing Said Nozzles". Any nozzle or nozzle / valve assembly which provides a means for releasing the mixture of detergent ingredients from the container and provides a foam is suitable for use in the present invention. The Precision Valve Company (Valve Précision in France) supplies a range of nozzle assemblies for various applications including shaving foams and carpet cleaners under various trade names including City®, Montego®, Power Jet®, Vulcan® and Visco®. Nozzles which disperse the foam both horizontally and vertically (when the container is held upright) are available. Metering nozzles which dispense a predetermined amount of foam are also available and useful in the present invention. Metering valves are disclosed in WO9108965 (Precision Valve Co) and EP-A 616953 (3M Co). In order for the apparatus to be effective in the method of the present invention it should deliver the foam at a rate of at least 3g per second of foam from the sealed container, more preferably at a rate of at least 10 g per second.

Method of Cleaning

The method of the present invention may be used to wash textile fabrics by hand (referred to herein as "hand-wash"). The foam is dispensed onto or around the textile fabrics to be washed, or dissolved (usually in water) to form a wash liquor. The whole surface of the fabrics is then exposed to the "neat" foam, or to the wash liquor. It is believed that

the foam ensures easy and even distribution of enzymes, either in "neat" form, or when dissolved to form a wash liquor, which promotes rapid and effective enzyme activity without causing fabric damage due to localised high concentration of enzymes.

The textile fabrics may be left to soak in the foam or wash liquor for anything up to several days, or even weeks. However it is preferred that the soaking time is between 1 minute and 24 hours, preferably between 5 minutes and 4 hours.

Normally the textile fabrics will be subsequently rinsed using clean water in order to remove any traces of detergent.

The method of the present invention is particularly well-suited to hand washing of delicate textile fabrics. In particular textile fabrics comprising high levels of wool or silk may be advantageously treated in this way. One particular benefit is a marked reduction in local fabric damage which may occur when conventional laundry processes are used. In conventional laundry processes the composition, the soiled textile fabrics and water are all brought together in a suitable container. At the beginning of the process there are very high local concentrations of enzymes as the composition begins to dissolve in the water, but it has been homogeneously distributed in the water. Such high local concentrations in solution, if they happen to be present on or close to the fabric can cause local fabric damage. This type of local fabric damage is avoided according to the method of the present invention. Because all of the enzymes are uniformly distributed throughout the large volume of the foam there are no local concentrations of active materials which might cause fabric damage.

A typical handwash composition will comprise some or all of the following components : surfactants (anionic, non-ionic, cationic, amphoteric, zwitterionic), detergent builders and chelating agents, soil release polymers, optical brightener, dye transfer inhibition polymer, perfume, enzymes, colorants.

Surfactants are preferably present at a level of from 10% to 90% by weight of the composition, preferably 20% to 80% of the composition, more preferably from 25% to 50% of the composition and most preferably about 30% by weight of the composition.

Detergent builders such as fatty acids, citric acid, succinic acid, phosphate, zeolite are preferably present at a level of from 10% to 90% by weight of the composition, preferably 10% to 50% of the composition, more preferably from 12% to 20% by weight of the composition.

Chelating agent such as phosphonate are preferably present at a level of from 0% to 5%, more preferably from 0.1% to 3% by weight of the composition.

An alternative washing method of the present invention may be used to wash textile fabrics in a conventional washing machine or, alternatively, if no added water is required, in a conventional drying machine (both cases referred to herein as "machine wash"). The foam of the present invention is simply dispensed into the drum of the machine either before or after the soiled textile fabrics have been loaded.

Most commercially available washing machines have automatic washing cycles. If water is added during the cycle most of the foam components will be dissolved or dispersed in the water, probably resulting in a layer of suds in the machine. As noted above, these suds which have a high water content and a low surfactant content should not be considered as foam within the meaning of the present invention.

The wash cycle may be completed by any combination of washing, rinsing, conditioning and/or drying steps, during any one of which additional wash or rinse additives may be introduced into the machine drum.

The compositions suitable for machine wash foams are similar to those described above for handwash foams.

Examples

Liquid laundry compositions were prepared by mixing the components according to the compositions in Table 1. Then each composition was packed into metal containers, each container having a nominal capacity of 405 cubic centimetres. The cans were filled with 250 ml of liquid detergent and then were pressurised with carbon dioxide while shaking, until it equilibrates to a can pressure of about 10 bars of carbon dioxide at about 20 °C.

All the cans are fitted with a 3 x 1.0 mm diameter standard valve (Code No. 045380 supplied by Valve Precision), without a dip tube and a straight whipped cream nozzle. In order to expel the foam out of the can, the can must be in an inverted position.

The cans were allowed to rest for a day at room temperature (about 20 °C) before use. Immediately before use, the cans were thoroughly shaken by hand to ensure homogeneity of the components inside the can.

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Example 1	
Alkyl sulphate	7.4
Alkyl ethoxy sulphate	6.4
Nonionic C12/C15 E7	10.6
NMG	4.0
Fatty acid	8.8
Citric acid	0.9
Propane diol	9.7
Ethanol	0.7
Monoethanolamine	6.8
Boric acid	4.5
Ca acetate	0.1
EDDS	1.3
Soil release polymer	0.2
PTMS	0.03
Ethoxylated TPP	0.3
PVNO	0.2
Perfume	1.6
PEG 200	25.0
ENZYME SYSTEM:	
Pure Protease protein	0.00075
Pure Cellulase protein	0.0001
Pure Lipase protein	0.004
Pure Amylase protein	0.009
Water	balance to 100
NMG is C12/C14 N-methyl glucamide. Ethoxylated TEP is ethoxylated tetraethylenpentamine. PVNO is polyvinylpyridin-N-oxide. PTMS is propyl trimethoxysilane.	

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1. A foam composition comprising a surfactant system and enzymes, characterised in that the foam composition comprises from 0.0001% to 0.005% pure protease enzyme protein by weight of the total foam composition.
- 50 2. A foam composition according to claim 1 wherein the composition comprises additional enzymes selected from the group consisting of cellulase, hemicellulase, peroxidase, amylase, gluco-amylase, xylanase, lipase, esterase, cur-
nase, pectinase, reductase, oxidase, phenoloxidase, lipoygenase, ligninase, pullulasase, tannase, pentosanase, malanase, β -glucanase, arabinosidase, chondroitinase, laccase, or mixtures thereof.
- 55 3. A foam composition according to claim 2 wherein the composition comprises additional enzymes selected from the group consisting of cellulase, amylase, lipase, or mixtures thereof.
4. A composition according to any of claims 1 to 3 further comprising from 0.00001% to 0.0005% pure cellulase

enzyme protein by weight of the total foam composition.

5. A composition according to claim 4 comprising from 0.00005% to 0.00025% pure cellulase enzyme protein by weight of the total foam composition.

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6. A packaged product for dispensing a composition according to any of claims 1 to 5, the packaged product comprising a sealed container, and a dispensing means, and further comprising a propellant gas, wherein the propellant gas comprises carbon dioxide, nitrous oxides, or mixtures thereof.

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7. A packaged product according to claim 6, the packaged product comprising an aerosol container and a foam dispensing nozzle.

8. A method of cleaning textile fabrics comprising the steps of :

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- (i) forming a foam composition, the foam composition having the composition of any of claims 1 to 5;
- (ii) dissolving or dispersing the foam in water to form an aqueous solution; and either subsequently or simultaneously
- (iii) agitating the cleaned textile fabrics in the aqueous solution.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 3075

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A,D	EP 0 677 577 A (PROCTER & GAMBLE) * claims * * examples *	1-8	C11D17/00 C11D3/386
A	FR 2 111 162 A (AKZO N V) * the whole document *	1-3,6,7	
A	US 3 781 212 A (SMILLIE W) * claims *	1-7	
A	US 4 954 286 A (SEPULVEDA RALPH R ET AL) * column 4, line 5 - line 15 * * examples * * claims *	1-3,6,7	
A	WO 95 10591 A (PROCTER & GAMBLE) * claims *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 8 April 1997	Examiner Pelli Wablat, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>4 : number of the same patent family, corresponding document</p>			

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